Dependence of magnetic properties of pellets of nominal composition $YBa_2Cu_3O_{7-x}$ on processing conditions

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We have studied the dependence of the magnetic properties of pellets of nominal composition $YBa_2Cu_3O_{7-x}$ on variations in preparation conditions. We find that rapid quenching of the pellets from annealing temperatures greater than 500–600 °C causes the formation of significant amounts of secondary phases. Two of these phases, Y_2BaCuO_5 and $BaCuO_2$, have magnetic moments of approximately $1.8\mu_B$ per Cu atom. We find that Y_2BaCuO_5 orders antiferromagnetically below 30 K whereas $BaCuO_2$ is paramagnetic down to at least 6 K. Eliminating these secondary phases by optimizing the processing conditions gives single-phase material (> 99.8% by mass) for which the magnetic susceptibility above the superconducting transition temperature is nearly independent of temperature. The magnitude of this susceptibility, after correction for ion-core diamagnetism, is enhanced by a factor of approximately 2 over the Pauli susceptibility estimated from the band-structure density of states, indicating the importance of electron-electron correlation effects.

INTRODUCTION

In recent months there has been considerable interest in the material $YBa_2Cu_3O_{7-x}$ following the discovery of its amazing superconducting properties.[1] Much work has been presented concerning the dependence of the superconducting properties of this material on details of its preparation conditions.[2–18] We present here a study of the magnetic susceptibility of a number of Y:Ba:Cu oxides of nominal 1:2:3 composition. Identically prepared pellets were annealed at different temperatures in several environments and subsequently cooled at different rates. In agreement with earlier reports,[19,20] we find a Curie-like susceptibility in the normal state for samples quenched at high rates from annealing temperatures above the tetragonal-to-orthorhombic transition temperature.[4] However, we find that this Curie contribution arises from secondary phases which increase in volume fraction with higher quench rates. For carefully prepared samples under optimized growth conditions, we find a nearly temperature-independent magnetic susceptibility in the normal state.

EXPERIMENT

The samples used in this study were prepared as follows. Appropriate mixtures of Y_2O_3, $BaCO_3$, and CuO powders (> 99.99% purity) were calcined and reacted at 900 °C for 12 h in flowing oxygen. They were subsequently reground and annealed again under similar conditions. The resulting powder was reground for a second time, pressed into pellets, and finally annealed for a third time. The pellets were approximately 12 mm in diameter and 2 mm thick. The pellets were then heat treated in various ways as described in Table I. The temperature of the final anneal, the annealing time, the annealing environment, and the rate at which the temperature of the pellet was decreased from the final anneal temperature were varied. The majority of the pellets were annealed in pure oxygen while others were annealed in argon, air, or vacuum. X-ray powder diffractometry was used to determine the phases in the pellets.

The resistance of the pellets was measured using a standard four-point probe, low-frequency lock-in technique utilizing silver paint contacts. Typically, currents of 100 μA were used. The superconducting transition temperature, T_c, is defined here as the temperature at which the resistance has dropped by a factor of 2 from that in the normal state. The width of the transition, ΔT_c, is defined as the difference between the onset temperature, T_0, and the temperature at which the resistance reaches zero. T_0 is the intersection of the extrapolated normal resistance curve and the tangent of maximum slope. The magnetic properties of the pellets were examined with an S.H.E. (Biomagnetic Technologies Inc.) superconducting quantum interference device (SQUID) magnetometer. Small rectangular blocks with an aspect ratio greater than 5 were cut from the pellets using a diamond saw and suspended in the magnetometer via thin copper wire or foil. The diamagnetic shielding signal, χ_{dia}, was measured by cooling the sample in nominally zero field, and then applying a small field (typically 20–100 Oe) at 6 K. The Meissner signal, χ_{Mei}, was obtained by subsequently cooling the sample in the same field from above T_c. The residual field in the magnetometer was measured using a small lead sphere and found to be of the order of 0.5–5 Oe. The demagnetizing factor was estimated to be no larger than 5% for all the samples studied.

RESULTS AND DISCUSSION

Normalized resistivity versus temperature curves for several representative samples from Table I are shown in Fig. 1. The highest transition temperature in this study

TABLE I. Heat treatment of $YBa_2Cu_3O_{7-x}$ pellets.

Pellet	Annealing temperature (°C)	Anneal time (h)	Annealing environment	Quench rate	T_c (K)	ΔT_c (K)
A	900	12	O	Slow[a]	91.5	3.0
B	900	12	O	Slow[a]	92.1	3.5
C	900	17	Vacuum[b]	Slow[a,c]	d	
D	920	12	Air	Fast[e]	87.3	9.0
E	900	12	O	Fast[e]	84.7	18.5
F	900	12	O	Fast[e]	61.0	11.6
G	900	12	O	Rapid[f]	36.7	39.6
H	700	4	O[g]	Slow[h]	93.1	3.4
I	700	17	Ar	Slow[a]	51	86
J	600	12	O	Slow[a]	90.5	5.0
K	600	12	O	Fast[e]	86.9	13.0
L	600	12	O	Rapid[f]	86.2	9.7
M	500	12	O	Rapid[f]	93.1	2.4
N	500	36	Ar	Slow[a]	50	20
O	500	36	Ar	Rapid[f]	≃4	i
P	400	12	O	Slow[a]	92.9	7.9

[a]Pellet allowed to cool in oven from T_{anneal} to about 200 °C in about 5 h.
[b]10^{-4} atm.
[c]Second anneal at 750 °C for 46 h.
[d]No superconducting transition observed.
[e]Pellet removed rapidly from oven and cooled on metal block.
[f]Pellet taken rapidly from oven and immersed in liquid nitrogen.
[g]2 atm.
[h]Cooled over ≃2 days at a controlled rate of 12 °C/h.
[i]Resistance finite at $T = 3.5$ K.

was obtained in the pellet that was annealed in 2 atm of oxygen at 900 °C and slowly cooled (≃100 °C/h) to room temperature. As can be seen from Table I, the quench rate plays an important role in determining T_c. Low quench rates give the highest T_c and smallest ΔT_c. However, the quench rate has much less effect on these properties for annealing temperatures below about 700 °C for $P_{O_2} \simeq 1$ atm. For these low anneal temperatures T_c and ΔT_c are not significantly affected by high quench rates. For example, Table I shows that for three samples annealed in oxygen and rapidly quenched by plunging the hot pellet into liquid nitrogen, there is a dramatic deterioration in the superconducting properties of the pellet annealed at 900 °C but very little change for pellets annealed at 600 and 500 °C. This behavior can be explained by the fact that, at equilibrium, the material undergoes a tetragonal to orthorhombic phase transition on cooling at around 700 °C in 1 atm of oxygen.[4,5] Depending on whether or not the anneal temperature is above or below this transition temperature determines the importance of the quench rate.[4] Annealing in argon over a wide range of annealing temperatures results in reduced T_c and severely broadened transitions independent of quench rate. High quench rates in argon cause deterioration in superconducting properties even for annealing temperatures as low as 500 °C. This is due to a shift in the tetragonal-to-orthorhombic transition to lower temperatures with decreasing partial pressure of oxygen.[5,6] The structure of the pellets was examined by x-ray powder diffractometry. Details of these data are reported in Ref. 3. The strongest peaks in the spectra for all the pellets correspond to those for $YBa_2Cu_3O_x$. The orthorhombicity of the unit cell decreases progressively with increasing quench rates and decreasing oxygen partial pressure. The spectra of the samples rapidly quenched from high temperatures have additional peaks indicating secondary phases. Comparison of these spectra with standards indicates the presence of $BaCuO_2$, Y_2BaCuO_5, and CuO.

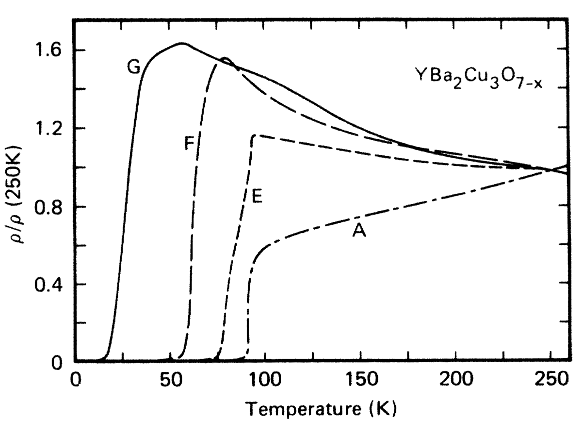

FIG. 1. Normalized resistivity vs temperature curves for various $YBa_2Cu_3O_{7-x}$ samples described in Table I. The resistivity is normalized to 1 at 250 K.

Meissner and diamagnetic shielding data as a function of temperature for the same samples shown in Fig. 1 are

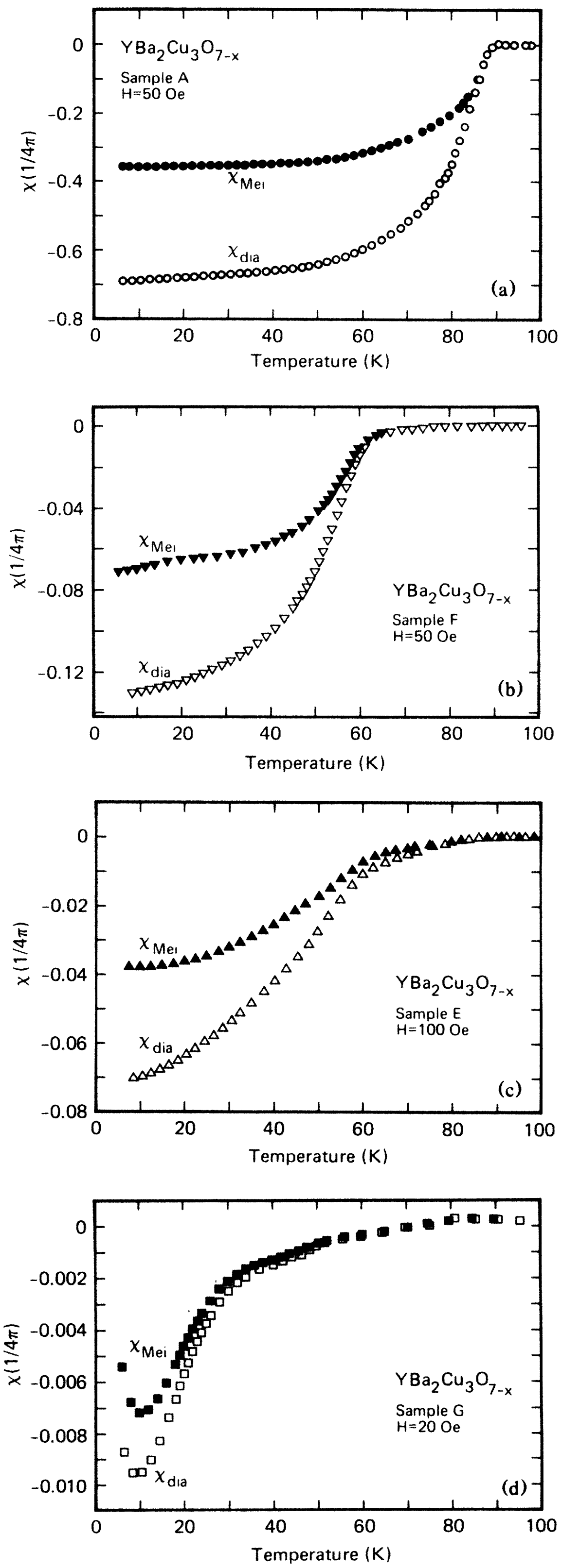

FIG. 2. Temperature dependence of the diamagnetic shielding susceptibility (χ_{dia}) and Meissner susceptibility (χ_{Mei}) in units of $1/4\pi$ for the same $YBa_2Cu_3O_{7-x}$ samples for which resistivity data are shown in Fig. 1. (a) Sample A, (b) sample F, (c) sample E, and (d) sample G. The magnitude of the applied field is given in the figure.

shown in Figs. 2(a)–2(d). Magnetic data for several pellets are summarized in Table II. Table II shows a wide variation in the magnitude of the magnetic signals, ranging from χ_{dia} of less than 1% of perfect diamagnetism ($1/4\pi$) for the sample quenched most rapidly from 900 °C to χ_{dia} of 86% of perfect diamagnetism in a slowly cooled sample. For samples A and F, the resistance curves and magnetic data are in good agreement and indicate similar transition temperatures of $\simeq$90 and $\simeq$60 K, respectively. In contrast, samples E and G show trace diamagnetism for temperatures up to about 90 K, even though the magnetic data show that the bulk of the sample undergoes a transition at a much lower temperature ($\simeq$60 and $\simeq$30 K, respectively). For sample E, the resistance curve suggests two distinct transitions, one near 90 K and the other close to 60 K, in accord with the magnetic data. As will be discussed, the normal-state magnetic susceptibility for these samples suggests multi-phase pellets. Thus, the resistive transition will depend upon the percolation path through the pellet. Indeed, for some pellets, we found no resistive transition but a change in magnetic susceptibility indicating that some parts of the sample were superconducting. For many of the pellets, in particular sample E, both the magnetic and resistance data suggest two distinct transition regions, one close to 90 K and a second close to 60 K. These results are consistent with the recent studies of Cava *et al.*[18] which show a nonlinear dependence of T_c on oxygen content. In particular, they find regions of oxygen content for which T_c is insensitive to the amount of oxygen and takes values of about 90 and 60 K, respectively.

TEM studies were made of sample G in order to correlate several breaks in this sample's susceptibility versus temperatures curve with the sample's microstructure. Specimens were prepared by crushing part of the pellet in ethanol. A small amount of this liquid containing submicron-thick fragments of the pellet material was pipetted onto a carbon grid. Studies of these fragments revealed three distinct "crystal types:" (1) twinned orthorhombic crystals, (2) orthorhombic crystals with a twinned interior and a defect-rich exterior shell, and (3) defect-rich tetragonal crystals. Figure 3 shows one example of the second crystal type. An electron diffraction pattern from the twinned interior of this grain exhibited streaking, indicating a different oxygen vacancy ordering

TABLE II. Magnetic data of $YBa_2Cu_3O_{7-x}$ pellets.

Pellet	T_c	χ_M[a]	χ_{dia}[a]	C (emu-K/g)	p[b]	f[c]
A	91.5	36	76	2.0×10^{-6}	0.06	0.2
B	92.1	18	86	6.6×10^{-5}	0.34	5.2
F	61	7.2	13	1.2×10^{-4}	0.45	9.5
E	84.7	3.8	7.0	2.2×10^{-4}	0.62	17.4
G	36.7	0.7	0.95	5.1×10^{-4}	0.96	40.3

[a]As percentage of $1/4\pi$.

[b]Effective number of Bohr magnetons per Cu assuming 100% of the pellet is $YBa_2Cu_3O_{7-x}$.

[c]Deduced weight percentage of secondary phases.

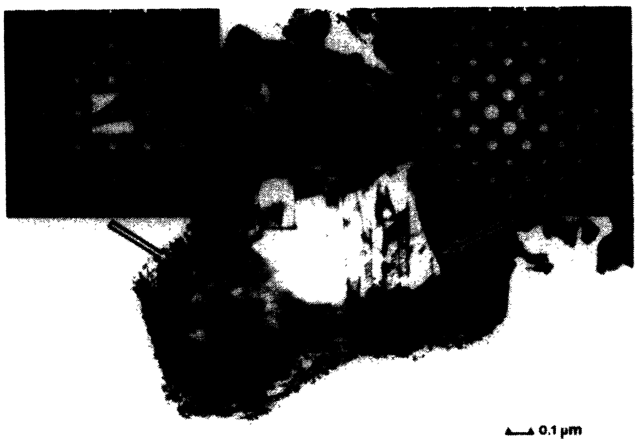

FIG. 3. TEM micrograph from an orthorhombic crystal in sample G with a twinned interior and a defect-rich outer shell. Streaks in the electron diffraction patterns indicate that the core material has additional short-range oxygen vacancy ordering. Grains varying from completely orthorhombic with no outer shell to completely tetragonal with poor crystal quality were observed in this sample. The small circular precipitates in the middle of the grain are secondary phases.

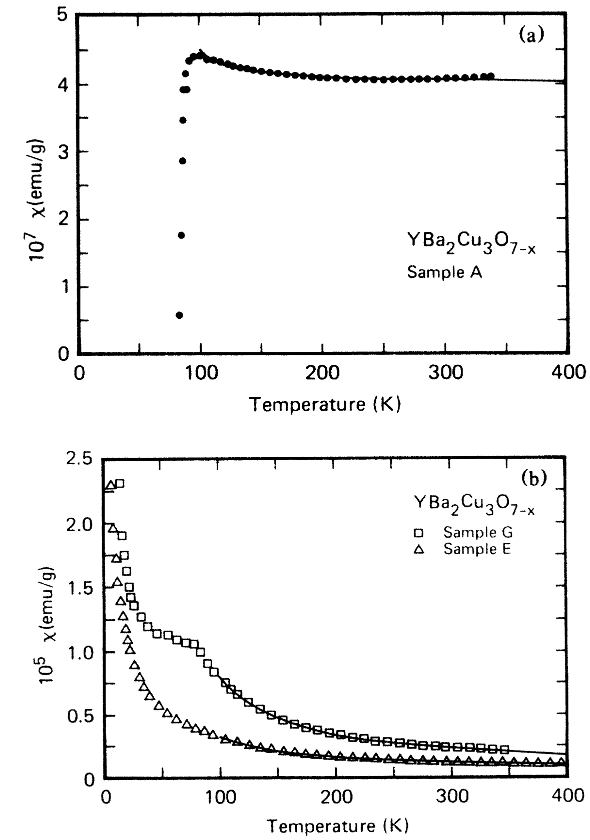

FIG. 4. Magnetic susceptibility vs temperature data for samples (a) A and (b) G and E. The data were measured at fields of 50, 0.99, and 50 kOe respectively. The solid lines are fits to a Curie-Weiss law with values of C given in Table II.

from that in crystals of type 1, whereas the highly defective exterior shell exhibited fainter streaking. We believe these three different microstructures can be correlated with the three breaks discernable at $\simeq 80$, $\simeq 50$, and $\simeq 30$ K in the susceptibility versus temperature curves shown for sample G in Fig. 2(d). The feature at 80 K arises from the orthorhombic grains. The kink at $\simeq 50$ K is probably associated with the orthorhombic grains that show different oxygen ordering. The most likely origin of the different ordering is a local doubling of the periodicity of the linear oxygen chains[21] (i.e., local removal of every other linear chain) in the $YBa_2Cu_3O_{7-x}$ structure. Lastly, the feature at 30 K is most probably associated with the highly defective crystals. These various crystal types presumably arose because crystals in the middle of the pellet experienced a reduced quench rate compared to those at the outside of the pellet.

Normal-state magnetic susceptibility data for samples A, G, and E are given in Figs. 4(a) and 4(b). The susceptibility increases rapidly with decreasing temperature for samples G and E and is well described by a Curie-Weiss law of the form $\chi = \chi_0 + C/(T - \Theta)$. The solid lines in Fig. 4(b) show fits to the data of this functional form with the values of C given in Table II. The magnitude of the Curie constant varies by more than a factor of 250 for the pellets in Table I. The magnetic susceptibility has the weakest temperature dependence (smallest C) in the pellets with the largest diamagnetic response below T_c. As shown in Fig. 4(a), sample A displays a nearly temperature-independent magnetic susceptibility. After subtracting a small Curie contribution, the temperature-independent susceptibility for sample A has a magnitude of $\chi_0 = 2.85 \times 10^{-4}$ emu/mole. Using Pascal's constants,[22] an ion-core diamagnetic contribution, χ_{core}, of -1.93×10^{-4} emu/mole can be estimated, giving a corrected value, $\chi_0^c = \chi_0 - \chi_{core}$, of 4.78×10^{-4} emu/mole. If we ignore electron-electron correlation effects, this value can be compared with the Pauli paramagnetism, χ_P, calculated from the expression $\chi_P = \mu_B^2 N(E_F)$, where $N(E_F)$ is the density of states at the Fermi level for both electron spin states. We also ignore the Landau diamagnetic contribution from the orbital motion of the conduction electrons. Since this term depends on the carrier effective mass[23] and there are several energy bands at the Fermi level with very different effective masses,[24-27] its determination is difficult. Using a value for $N(E_F)$ of $\simeq 6.5$ states/eV cell obtained from the band-structure calculation by Herman, Kasowski, and Hsu,[24] we can estimate $\chi_P = 2.1 \times 10^{-4}$ emu/mole. Similar values for $N(E_F)$ are reported by other researchers.[25-27] Thus, the measured susceptibility is enhanced over the Pauli term by a factor of about 2.3. Note that considerably larger enhancement factors have been reported for the $La_{1-x}Sr_xCuO_4$ compounds.[28] Using an expression[29] for the enhancement factor of $1/[1 - N(E_F)U]$ where U is the Hubbard intra-atomic energy, we obtain a value for U of about 0.09 eV. However, the above expression for the enhancement factor is only valid where $N(E_F)U \ll 1$. Since we find $N(E_F)U \simeq 0.6$, the validity of this analysis is in doubt and suggests that electron-electron correlation effects must be included.[30]

As discussed earlier, x-ray spectra show evidence for small amounts of Y_2BaCuO_5, $BaCuO_2$, and CuO in the pellets rapidly quenched from high temperatures. The crystal structures for these compounds are known.[31,32] We find a rough correlation between the amount of these secondary phases in our samples and the magnitude of the Curie constant. In order to estimate the amount of these secondary phases present, we prepared and measured the magnetic susceptibility of pellets containing only Y_2BaCuO_5, $BaCuO_2$, and CuO. Data for these reference compounds are shown in Fig. 5 and the fitted Curie constants and Curie-Weiss temperatures are tabulated in Table III. Data are also included for a multiphase sample of nominal composition Ba_3CuO_4 for reference purposes. CuO has a small susceptibility and appears to order antiferromagnetically below about 240 K. These results are in good agreement with those reported in Ref. 33. The Curie constant for $BaCuO_2$ is in reasonable agreement with that found in an earlier study.[31] We find that the green compound Y_2BaCuO_5 orders antiferromagnetically below about 30 K with a magnetic moment on the Cu atom similar to that for $BaCuO_2$ and close to that for Cu^{2+}. The magnetic susceptibility curve for this compound displays a slight anomaly near 90 K, suggesting a small amount of the $YBa_2Cu_3O_{7-x}$ phase. The observation of antiferromagnetism in Y_2BaCuO_5 explains the results of Sun *et al.*[20] who reported the existence of antiferromagnetism in the $YBa_2Cu_3O_{7-x}$ compound. Moreover, small amounts of these secondary phases will give rise to a substantial Curie paramagnetism, explaining early reports of a Curie paramagnetism in the $YBa_2Cu_3O_{7-x}$ compound.[19] Indeed, the Curie term can be used to determine the mass fraction of secondary phases from the measured Curie constants for these phases, assuming a disproportionation of $YBa_2Cu_3O_{7-x}$ into Y_2BaCuO_5, $BaCuO_2$, and CuO. Using this method, we found that the proportion of secondary phases in our $YBa_2Cu_3O_{7-x}$ pellets ranged from 0.2 to 40 wt.% depending on processing conditions (Table II).

TABLE III. Magnetic data of standard compounds.

Pellet	Θ (K)	C (emu-K/g)	p[a]
$BaCuO_2$	19.0	1.8×10^{-3}	1.82
Ba_3CuO_4	14.0	7.4×10^{-4}	1.78
Y_2BaCuO_5	−49.3	9.3×10^{-4}	1.85

[a]Effective number of Bohr magnetons per Cu.

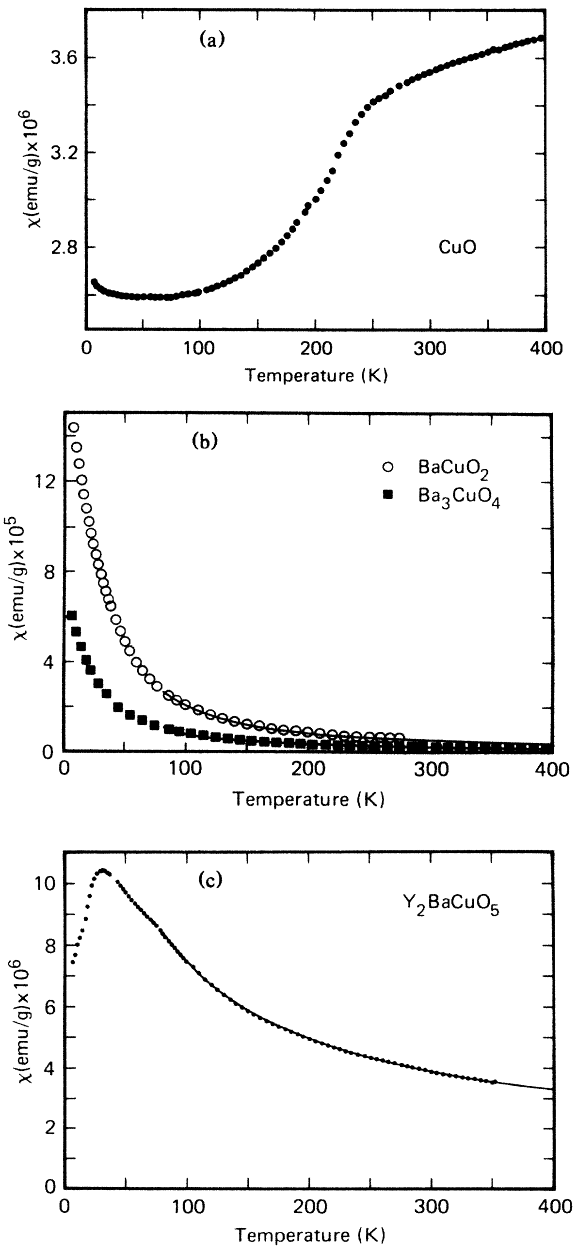

FIG. 5. Magnetic susceptibility vs temperature data for (a) CuO, (b) $BaCuO_2$ and Ba_3CuO_4, and (c) Y_2BaCuO_5. The solid lines are fits to a Curie-Weiss law with values of C and Θ given in Table III.

SUMMARY

We have studied the dependence of the magnetic properties of a number of pellets of nominal composition $YBa_2Cu_3O_{7-x}$ on preparation conditions. The magnetic behavior is most sensitive to the rate of temperature decrease for annealing temperatures above 500–700 °C. Features in the susceptibility versus temperature curves can be related to various distinct microstructures found in quenched samples. For pellets with the largest diamagnetic shielding and Meissner signals we find the magnetic susceptibility of $YBa_2Cu_3O_{7-x}$ is nearly independent of temperature for temperatures above T_c. The magnitude of this susceptibility after correction for ion-core diamagnetism and ignoring the Landau diamagnetic term is about two times larger than a Pauli susceptibility estimated from the band-structure density of states at the Fermi level. For pellets with a reduced diamagnetic response below T_c, we find a significant Curie contribution which increases as the diamagnetic response decreases. We attribute this contribution to secondary phases, primarily Ba_2CuO_2 and Y_2BaCuO_5. We find that the latter phase orders antiferromagnetically below 30 K whereas the former shows no magnetic ordering down to 6 K. The size of the Curie term indicates as much as 40 wt.% of the sample is comprised of secondary phases depending on preparation technique. We suggest that early reports of antiferromagnetism and Curie paramagnetism in pellets of nominal composition $YBa_2Cu_3O_{7-x}$ arise from these magnetic secondary phases.

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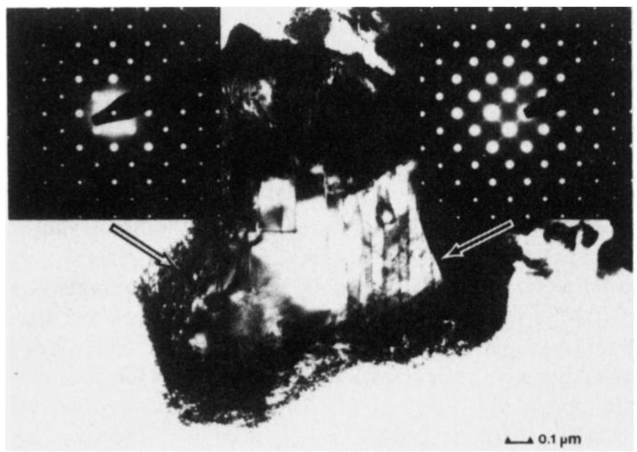

FIG. 3. TEM micrograph from an orthorhombic crystal in sample *G* with a twinned interior and a defect-rich outer shell. Streaks in the electron diffraction patterns indicate that the core material has additional short-range oxygen vacancy ordering. Grains varying from completely orthorhombic with no outer shell to completely tetragonal with poor crystal quality were observed in this sample. The small circular precipitates in the middle of the grain are secondary phases.